

PATENT SPECIFICATION

(11) 1246 645

1246 645

NO DRAWINGS

(21) Application No. 43924/68 (22) Filed 16 Sept. 1968

(45) Complete Specification published 15 Sept. 1971

(51) International Classification C 08 g 20/20//20/38, 33/02

(52) Index at acceptance

C3R 22C10 22C12 22C25 22C33B 22D1A2 22D1AX
22D2A2 22D2BX 22L1B 22L2X 22MX 22N1B
22NX 22PX 22T2

(72) Inventors VASILY VLADIMIROVICH KORSHAK
ALEXANDR ANDREEVICH IZYNEEV and
VALENTINA GEORGIEVNA SAMSONOVA



(54) METHOD OF PRODUCING POLYAMIDES

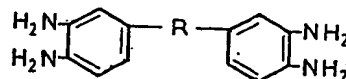
(71) We, BURYATSKY INSTITUT
ESTESTVENNYKH NAUK, a Corporation orga-
nised and existing under the Laws of the
Union of Soviet Socialist Republics of 35
Kirova, Ulan-Ude, Union of Soviet Socialist
Republics do hereby declare the invention for
which we pray that a Patent may be granted
to us, and the method by which it is to be
performed, to be particularly described in
and by the following statement:—

The present invention relates to the pro-
duction of polymers. More particularly, the
invention is concerned with polyamides pos-
sessing improved light and heat resistance.

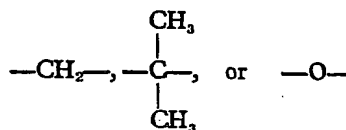
Copolymers containing both benzoxazole
and amide structures have been previously
disclosed in British Patent No. 811,758. The
polymers disclosed in that Patent are, how-
ever, characterised as being polybenzoxazoles,
the copolymerisation therein of monomers
such as hexamethylenediamine/dicarboxylic
acid being an optional modification thereof.
In contrast, the present invention is concerned
with polymers which are characterised as
being polyamides of hexamethylenediamine
and a dicarboxylic acid, heterocyclic struc-
tures being introduced in an amount sufficient
only to enhance the stability of such polymers
against light, heat and hydrolysis, but in-
sufficient to change their character and field of
application from those of polycarbonamides of
hexamethylene diamine to those of poly-
benzoxazoles.

According to the present invention there
is provided a method of producing a poly-
amide by the polycondensation of a mixture
of hexamethylenediamine and a dicarboxylic
acid or its diphenyl ester in the presence of
up to 6% mol, based on total reactants, of
an aromatic tetra-amine of the general for-
mula:—

[Price 25p]

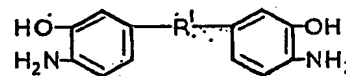


where R=a direct carbon to carbon valency
link.

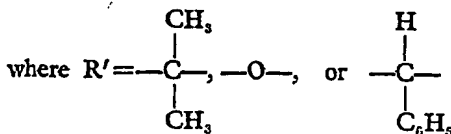
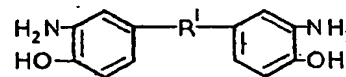


50

or an aromatic bis - o - aminophenol of the
general formula:—



or



where R'=—C—, —O—, or —C—
CH₃ C₆H₅

in a stream of inert gas while heating to 55
180—260° C.

To increase the molecular weight, the poly-

amide obtained may be additionally heated in vacuo (1 mm mercury) at 260—280° C.

- 5 A general method of producing polyamides according to the present invention is embodied as follows.

- 10 Before beginning the reaction of polycondensation, the initial components are thoroughly comminuted, mixed and charged into a condensation flask through which a clean inert gas is blown, the flask being alternately filled and evacuated. The reaction flask is then placed in a bath preliminarily heated to 180°C, after which the reaction mixture, which forms a melt, is heated to the temperature of the synthesis. The aromatic tetra-amine or bis - o - aminophenol may be added with the initial monomers or after the poly-
15 amide melt has formed.

- 20 Polyamides prepared in the presence of aromatic tetra-amines or bis - o - amino - phenols contain benzimidazole or benzoxazole groups. Said groups are more resistant to chemical reagents, light and heat than aliphatic groups. For that reason they impart to polymers improved properties compared with the unmodified polyamides.

- 25 The polyamides manufactured, according to the present invention, can be used for lengthy periods at temperatures up to 150° C, possess
30 50—100% higher light resistance than polyamides now commercially available and are more resistant to concentrated mineral acids, e.g. they are only partially hydrolyzed by concentrated hydrochloric acid.

- 35 The method according to the present invention is illustrated by the following examples, in which the percentages given are percentages by weight unless otherwise stated.

EXAMPLE 1

- 40 A mixture of 1.05 of hexamethylene - diamine (0.009 mol), 3.00 g (0.01 mol) of diphenyl adipate and 0.21 g (0.00098 mol, or 4.9% mol. based on total reactants) of 3, 3' - diaminobenzidine is heated in a stream
45 of inert gas at 180—260° C for 3 hours. After the formation of a melt, the reaction is continued in vacuo (1 mm Hg) at 270° C for another 3 hours. The polyamide has an inherent viscosity of 0.61 in tricresol (0.5%
50 solution at 20° C). The polymer is crystalline and soluble in tricresol, formic acid and chloral hydrate.

EXAMPLE 2

- 55 A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine and 3.54 g (0.01 mol) of diphenyl sebacate is heated in a stream of inert gas at 180—250° C for 2 hours, whereupon 0.22 g (0.001 mol. or 5% mol. based on the total reactants) of 3, 3' - diamino -
60 benzidine is added and the reaction is continued for another 3 hours. The polyamide has an inherent viscosity of 1.02 in formic acid (0.5% solution in 90% formic acid

at 20° C). The polymer is crystalline and soluble in formic acid and tricresol.

65 The tensile strength of a film formed from the above polyamide is lowered 8.3% when exposed to the air and sunlight for four months in summer; the tensile strength of polyamide film produced by a prior art method is lowered 25% under the same conditions. The reduction in tensile strength of polyamide film produced in the presence of a bis - o - aminophenol, i.e. 4, 4' - dihydroxy-
70 3, 3' - diaminodiphenylpropane (Example 4), in the same conditions is 7.8%. Said polyamide is partially hydrolyzed when acted on by concentrated hydrochloric acid at 80° C for one hour. When the hydrolysate is diluted with water, a polyamide is precipitated which has an inherent viscosity of 0.2 in formic acid (0.5% solution in 90% formic acid at 20° C). Judging by the results of thermogravimetric analysis, the loss in weight of said polyamide at 350° C is 7.3%, whereas the loss in weight of polyamide produced by the prior art
85 method is 22.7%.

EXAMPLE 3

A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.54 g (0.01 mol) of diphenyl sebacate, 0.1 g (0.00044) mol of the tetra-amine of diphenyl methane and 0.15 g (0.00065 mol) of the tetra-amine of diphenyl oxide is condensed by the method described in Example 1. The mol. percentage of the last two compounds based on total reactants is 5.45. The inherent viscosity of the polyamide is 0.60 in tricresol (0.5% solution at 20° C). The polymer is crystalline and soluble in formic acid, tricresol and chloral hydrate.
100

EXAMPLE 4

A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine and 3.54 g (0.01 mol.) of diphenyl sebacate is heated in a stream of inert gas at 180—260° C for 3 hours, whereupon 0.24 g (0.00098 mol, or 4.95 % mol. based on total reactants) of 3, 3' - diamino - 4, 4' - dihydroxydiphenylpropane is added and the reaction continued at 260—
110 270° C for another 2 hours. The inherent viscosity of the polyamide is 0.51 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in formic acid and tricresol.
115

EXAMPLE 5

A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.00 g (0.01 mol.) of diphenyl adipate and 0.22 g (0.0009 mol. or 4.5 mol. % based on total reactants) of 3, 3' - diamino - 4, 4' - dihydroxydiphenylpropane is heated in a stream of inert gas at 180—
120 260° C for 3 hours. After the formation of a melt the reaction is continued in vacuo

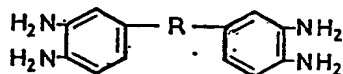
- (1 mm Hg) at 265° C for another 3 hours. The inherent viscosity of the polyamide is 0.65 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in m-cresol, tricresol and formic acid.

EXAMPLE 6

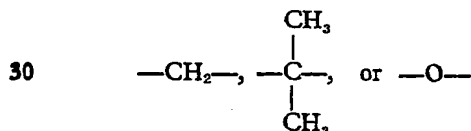
- A mixture of 1.05 g (0.009 mol.) of hexamethylenediamine, 3.54 g (0.01 mol) of diphenyl sebacate, 0.10 g (0.00043 mol.) of 3, 3' - diamino - 4, 4' - dihydroxydiphenyl methane and 0.14 g (0.00061 mol) of 3, 3' - diamino - 4, 4' - dihydroxydiphenyl oxide is condensed by the method described in Example 5. The mol. percentage of the last two compounds based on total reactants is 5.2. The inherent viscosity of the polyamide is 0.58 in m-cresol (0.5% solution at 20° C). The polymer is crystalline and soluble in m-cresol, tricresol and formic acid.

WHAT WE CLAIM IS:—

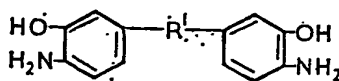
1. A method of producing a polyamide comprising the polycondensation of hexamethylenediamine and a dicarboxylic acid or its diphenyl ester in the presence of up to 6% mol, based on total reactants of an aromatic tetraamine of the general formula:—



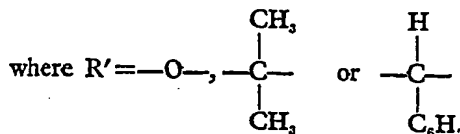
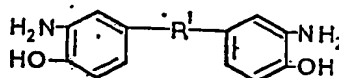
where R=a direct carbon to carbon valency link,



or an aromatic bis - o - aminophenol of the general formula:—



or



in a stream of inert gas while heating to 180—260° C.

2. A method as claimed in claim 1, wherein, after heating in a stream of inert gas, the reaction mixture is heated in vacuo at 260—280° C.

3. A method as claimed in claim 1 or 2, wherein the hexamethylenediamine and the dicarboxylic acid or its diphenyl ester are preheated to form a melt after which the tetra-amine or aminophenyl is added.

4. A method as claimed in claim 1 or 2 wherein the tetra-amine or aminophenol is added with the hexamethylenediamine and the dicarboxylic acid or its diphenyl ester, and the mixture is subsequently preheated to form a melt.

5. A method of producing a polyamide substantially as hereinbefore described in any one of Examples 1 to 6.

6. A polyamide when produced by the method as claimed in any preceding claim.

MARKS & CLERK,
Chartered Patent Agents,
Agents for the Applicant(s).